

Sequestration of CO₂ in magnesium silicates, in Western Macedonia, Greece

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ABSTRACT

Carbonation of magnesium seems to be an interesting option for long term storage of captured CO₂. This paper provides an approach to sequestration of carbon dioxide in magnesium silicates using ultramafic rocks from the mountain of Vourinos, in Western Macedonia, Greece. For the experimental procedure five samples were used, consisted of dunite, hartzburgite and pyroxenite. The carbonation method chosen is the aqueous scheme. The results showed low (only about 10% of the stoichiometrically possible amount) transformation into magnesium carbonates for the majority of the samples. Insufficient reaction time, the particle size, or improper choice of reaction conditions are may be some of the reasons for the small amounts of carbonation observed. Further studies are needed in order to identify the various issues that were responsible.

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1. Introduction

Fossil fuels are the dominant form of energy utilized in the world (86%) and nowadays, they are facing a major challenge due to the large amounts of CO₂ released into the atmosphere as a result of combustion. They account for about 75% of current anthropogenic CO₂ emissions (IPCC—Intergovernmental Panel on Climate Change, 2001). It is a fact that in the early years of the 21st century CO₂ continued an upward trend. It is well known that the CO₂ is a greenhouse gas, and in such large and ever growing amounts can have serious effects on the global climate.

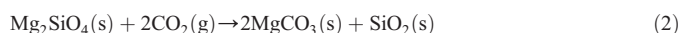
Many articles have been published concerning carbon capture and storage (CCS) technologies, stating the reasons for it and the different approaches for achieving it. In this paper we present a preliminary investigation of a possible storage method for Greece, that of mineral carbonation. Examples of other possible sequestration methods, but not discussed here, are geological storage in underground permeable and porous formation, ocean storage, and storage in unminable coal seams.

Compared to these other storage options, mineral carbonation has some advantages such as theoretical power generation as it is an exothermic reaction, the large storage capacity since there is an abundance of magnesium and calcium silicate deposits worldwide, and the thermodynamic stability of the resulting solid products. As a result, the storage method is permanent, safe, and does not require site monitoring (Goff and Lackner, 1998, Lackner et al., 1995).

Alkaline-earth oxides, such as magnesium oxide (MgO) and calcium oxide (CaO), are present in large amounts. The former is also available at high concentrations in naturally occurring silicate minerals, such as serpentine and olivine (Goff and Lackner, 1998). Carbonation of these minerals traps CO₂ as environmentally stable solid carbonates, which would provide storage capacity on a geological time scale. Carbonation of serpentine mineral can be described with the following overall chemical reaction (Eq. (1)):



In the case of olivine the reaction is:



The natural carbonation of magnesium silicate minerals is very slow, which means that the carbonation reaction must be accelerated considerably to be a viable large-scale disposal method for captured CO₂ (Teir et al., 2007).

Greece, as the second largest producer of lignite within the European Union, generates almost 93% of its electrical power requirements from fossil fuels, with lignite accounting for about 64% of the total (Koukoulas, 1998). The largest of Public Power Corporation's lignite-fired power plants are in the region of Western Macedonia and are associated with the Ptolemais–Amynteo lignite centre (LCPA). These plants, Table 1, account for 80% of the total annual CO₂ emissions (~43,000 ktons/yr CO₂) from the Greek lignite-fired electricity generation sector (Psomas, 2006).

The minerals that are selected to be more suitable for the binding of CO₂ are the ultramafic rocks because the deposits are both large and very rich in magnesium oxides (~35–55%). These oxides are

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Table 1The main power plants in Western Macedonia Region and their CO₂ emissions in 2005.

Power plant	Installed capacity (MW)	Emissions (kton CO ₂ /yr)
PPC S.A., TPS Ag. Dimitriou	1595	13,629
PPC S.A., TPS Kardias	1250	9815
PPC S.A., TPS Ptolemaidas	620	3488
PPC S.A., TPS Amyndaïou	600	5124
PPC S.A., TPS Florinas	330	1956
PPC S.A., TPS Liptol	43	358
Total		34,371

chemically bound with other oxides in the form of a silicate matrix. The resulting rocks can be found within the ophiolite complexes.

Although carbonation of calcium oxide is easier, the use of magnesium-based minerals (dunites, peridotites, and serpentinites) is favored because they are available worldwide in large amounts and in relatively high purity (Huijgen and Comans, 2003). The amount of oxide required to bind CO₂ from burning 1 ton of carbon, additionally, favors magnesium oxide at 3.3 tons compared to 4.7 tons of calcium oxide (Lackner et al., 1995).

2. Geological settings

The Vourinos ophiolite complex extends SW of the city of Kozani and covers an area of approximately 450 km². It is known for its well-developed ophiolite sequence and the significant chromite deposits. The ophiolite rocks of Vourinos are thrust over Jurassic continental platform carbonates and pelitic sediments, and are unconformably overlain by Upper Cretaceous rudist-bearing limestones. The peridotites (mainly harzburgites) comprise ca. 85% of the sequence by volume (Liati et al., 2004). The area was selected in order to provide the samples for the carbonation experiments because of its geology and its vicinity to the CO₂ point sources (Ptolemais included).

The complex consists of a northern and a southern block. The blocks are separated by an E–W trending slip fault which passes near the villages of Chromion and Vari (Fig. 1). In more detail, the northern block is comprised mainly of harzburgites with interlaminated dunites (Ross et al., 1980). Rocks in the northern block are relatively unserpentinized (<15%) except along the fault zone. The geology in the southern block is similar to the northern block with interlayered harzburgite and dunite comprising nearly two-thirds of the block. The layers of dunite vary in thickness from about 10 to 200 m. In both blocks, the limited serpentinization that is observed is a late low temperature phenomenon possibly related to the final transport phase at very high crustal levels leading to the complexes' positions (Ross et al., 1980).

The largest dunite deposits of Vourinos Complex are those of Xerolivado whose length is greater than 5 km (Dabitzias and Rassios, 2000). In addition, fresh slightly serpentinized dunites and harzburgites occur in a belt 20 km long and 0.5 to 1 km wide, between the basal thrust sole of the ophiolite and the zone of chromites (Dabitzias and Rassios, 2000).

3. Feasibility of mineral sequestration in Western Macedonia

According to chemical analyses carried out by the Institute of Geology & Mineral Exploration, olivine, chromite, and orthopyroxene are the main mineralogical phases of these deposits, with the orthopyroxene accounting for ~8% of the total. The range of the major elements' concentration is listed in Table 2 (IGME, Greece). These Mg-rich silicate minerals with an average MgO content of ~45 wt.% and little pyroxene represent desirable ores for the chemical fixation of CO₂ (Lackner et al., 1997).

We collected a number of samples from different regions of the Vourinos Complex. Of these, 5 representative samples were selected and

used in subsequent carbonation experiments. Their places of origin are indicated in the map (Fig. 1) and their pictures prior to the experimental work are given in Fig. 2. The samples were comprised of one pyroxenite (S1), two dunites (S3, S7) and two harzburgites (S2, S4).

It has been estimated that the amount of CO₂ that the Vourinos complex can sequester is approximately 24,648 Mtons CO₂, assuming 100% carbonation. To calculate this, we took into account the average density of the complex (for harzburgite and dunite that are also our sample materials), which is around 3.5 g/cm³, their average weight fraction of MgO (wf = 0.43) and also the fact that 1 mol of MgO has a mass of 40.3 g and 1 mol of CO₂ has a mass of 44 g.

4. Methods

From a review of the literature we can see that different methods have been proposed for mineral CO₂ sequestration. The majority of them are a combination of a pre-treatment and a carbonation process. The carbonation process that was selected is the aqueous scheme with the use of additives in order to accelerate the reaction, as will be explained later.

The first step that was taken was the preparation of the samples. At a minimum, the so called pre-treatment always consists of at least size reduction. In addition, and depending on source material, the pre-treatment may also include magnetic separation and/or thermal treatment. Their common goal is to increase reaction rate. Decreasing the size of the rock particles increases the reactive surface available for carbonation. Thermal treatment is often used for pre-treating serpentinites. Oxidation of magnetite during thermal pre-treatment lowers the reactivity of the material and can be largely prevented by magnetic separation.

The samples selected for experimental work were ground so as to pass, in a good proportion, a No. 200 sieve and then also a No. 230 sieve, which respectively correspond to nominal particle sizes of 0.074 and 0.063 mm. As the samples were not serpentines, no thermal pre-treatment was performed. However, following the grinding, a magnetic separation was still performed to prevent any possible reaction rate degradation from any magnetite present². The weight of the pulverized samples, before the carbonation, is shown in Table 3.

The actual carbonation reactions of our samples were conducted in the facilities of our collaborating institute (Los Alamos National Laboratory), as they already had the necessary equipment including many years of previous experience on the subject. A 1.8 l Parr autoclave, which contained an entrained gas stirrer, was used. It was interfaced with a Haskel gas booster pump to pressurize the CO₂ up to 158.6 bars (2300 psi).

In order to run the carbonation experiments, 85 g of starting material (in powdered form) was used, except for sample 2 where only 83.5 g of material was available. The rock powder was added to a solution consisting of deionized water (3/4 l), 3/4 mol NaCl and 0.48 mol NaHCO₃. This resulted in a 1 M NaCl, 0.64 M NaHCO₃ solution.

Once the solution and rock powder were put in the autoclave, the autoclave was closed. Then, the system was flushed with several exchanges of CO₂ gas, prior to fully sealing the system at local atmospheric pressure (0.79 bar). Once sealed, the stirrer was started and run at 300 rpm. The system was then heated to ~155 °C which typically took about an hour. The autoclave pressure at this point was several atmospheres as it was above the boiling temperature of water. When temperature reached 155 °C, the stirrer speed was increased to 900 rpm and CO₂ from a gas bottle was injected through the booster pump into the autoclave. It took about 30 min for the system to reach

² Past experimental work with serpentine samples showed lower reaction rates following heat pre-treatment (~600 °C) due to oxidation of magnetite and formation of a hematite barrier. (O'Connor et al., 2000a) To avoid any possibility of similar issues due to the water environment, magnetite separation was performed although no high temperature heat pre-treatment was performed on our samples.

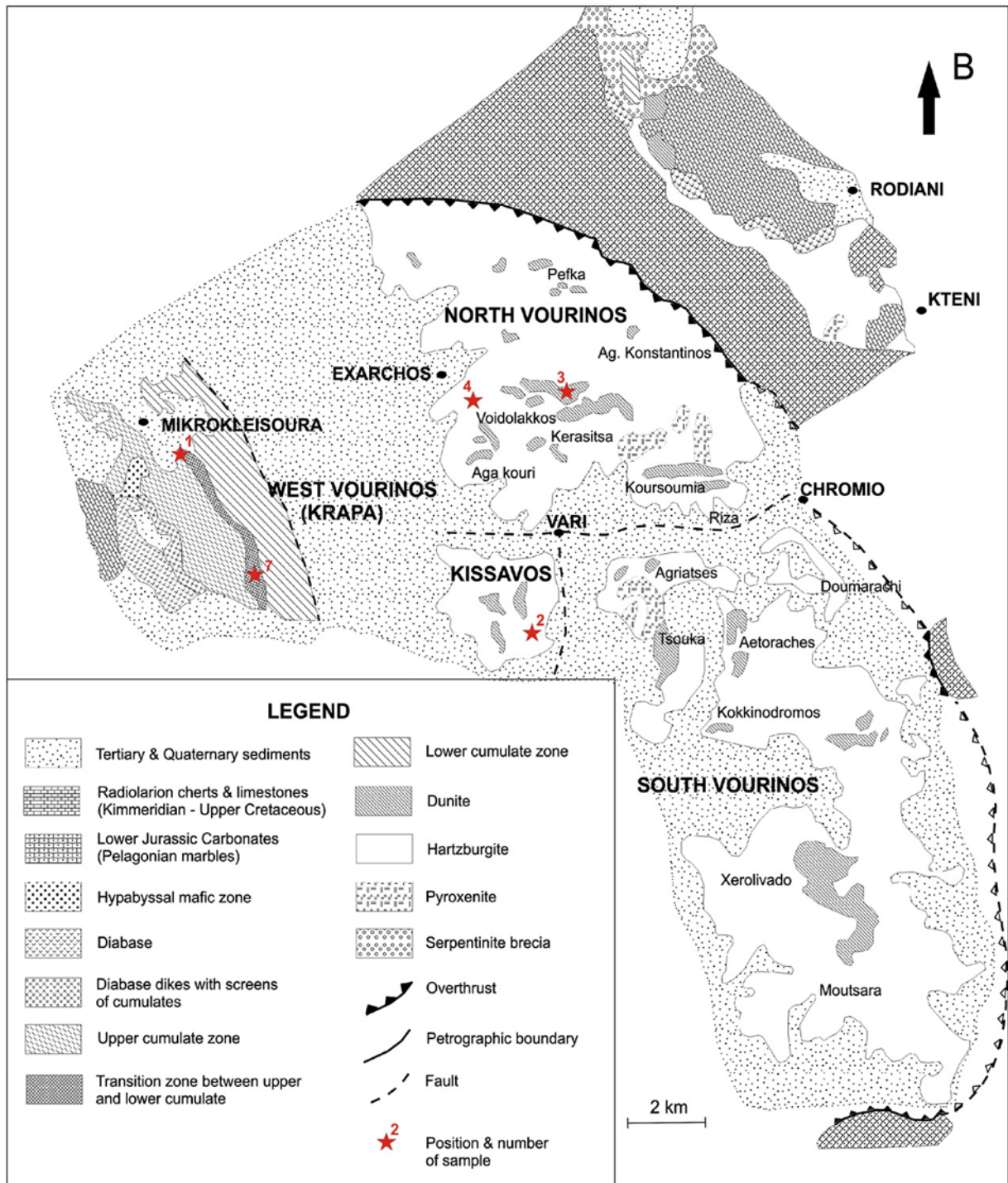


Fig. 1. Simplified geologic map of Vourinos and Rodiani ophiolite complexes showing the sampling locations.

a total absolute pressure of 158.6 bars using the booster pump. If (due to a slow gas leak in the autoclave system or removal of CO₂ through reaction) the gas pressure inside the vessel dropped down to 151.7 bars, the gas pressure was boosted back up to 158.6 bars with the Haskel pump. After about 2 h and 5 min at temperature and high pressure, the heating coil was turned off and cold water was run through the cooling tubes of the autoclave.

As the system cooled, the gas pressure of course dropped. When the temperature was about 40 °C, the residual CO₂ gas pressure (~70 bars) was slowly vented. When the venting started, the stirrer speed was also reduced to 300 rpm, and finally stopped when local atmospheric pressure was reached. The combined cooling and venting

time was approximately 20 min. The autoclave was then opened and its contents were recovered using some flushing/rinsing with limited amounts of deionized water. The resulting volume of the solution plus rock powder was typically slightly more than 1 l. The solution was then allowed to settle overnight and the supernatant was removed.

Fresh deionized water was then added to the residual slurry to yield a volume of ~2 l. This was allowed to settle overnight for the second time and the supernatant was again removed. The resulting slurry was then allowed to dry at a temperature of ~50 °C using a heating plate. The samples following this procedure are shown in Fig. 3. Small amounts of reacted samples were typically lost due to imperfect flushing of the autoclave and material removed as part of the “supernatant”.

Table 2

The range of the chemical composition (wt.%) of ultramafic rocks from Vourinos Complex.

SiO ₂	40.64–42.78
Al ₂ O ₃	0.38–0.57
Fe ₂ O ₃	8.00–8.72
CaO	0.28–0.98
MgO	43.52–46.52
K ₂ O	0.01
Na ₂ O	0.03
MnO	0.10–0.13
TiO ₂	0.01
Cr ₂ O ₃	0.34–1.59
NiO	0.31–0.34
LOI	1.50–3.37

5. Results

Following size reduction and magnetic separation, the unreacted starting rock powders were analysed through X-ray Diffraction (XRD) in order to determine the minerals that they contain. Those are augite,

Table 3

The weights of the samples before and after the mineralization process.

Sample	Weight before the mineralization (g)	Weight after the mineralization (g)
S1	85,033	82,890
S2	83,427	85,766
S3	85,000	85,950
S4	84,429	87,950
S7	85,009	88,560

diopside, lizardite, clinochrysotile, forsterite, olivine, and enstatite. All of the above minerals are typical for the ultramafic rocks.

In the aqueous scheme, the CO₂ reacts at high pressures with some of the silicates of the rock powder in the solution. A plausible reaction path (O'Connor et al., 2000b) involves the following steps: first, CO₂ is dissolved in distilled water to form carbonic acid, which dissociates to bicarbonate and H⁺:

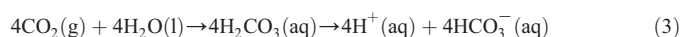


Fig. 2. The samples before the pre-treatment for the carbonation experiments.

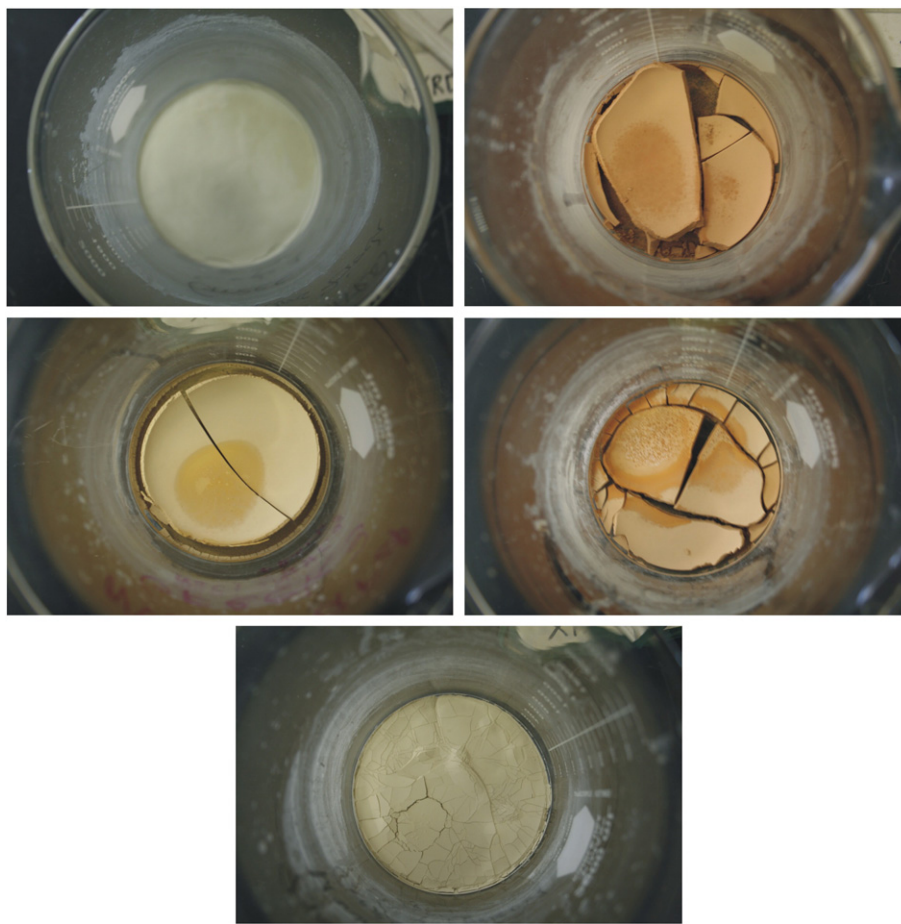
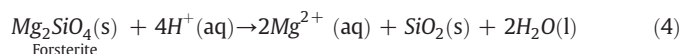
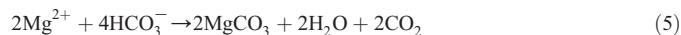


Fig. 3. The dry product material. The samples are in the same order as in Fig. 2 (i.e. S1, S2, S3, S4 and S7).

Then, mineral hydrolysis liberates Mg^{2+} cations from the olivine matrix with co-production of silica acid or free silica and water:



Finally, the Mg^{2+} cations react with bicarbonate ions to form magnesite:



In order to increase the reaction rate, a mixture of $\text{NaHCO}_3/\text{NaCl}$ was added to the water. The sodium bicarbonate (NaHCO_3) is a more effective CO_2 carrier (O'Connor et al., 2000a), significantly increases the HCO_3^- concentration, and affects the solution pH, both favoring carbonate precipitation. Moreover, the chlorine ions associated with the NaCl likely enhance the solubility of magnesium by creating soluble complexes (MgCl_2 , MgCl_3^- , MgCl_4^{2-}), (Huijgen and Comans, 2003).

After the experiments, the samples were subject to another XRD analysis in order to identify the minerals that were formed. From patterns observed, it can be seen that even though the bulk of minerals were not converted, a small proportion of magnesite was formed. Magnesite exists in only four of the five samples (S1 does not contain MgCO_3).

In order to determine the fractional magnesite production, a semi-quantified analysis was attempted with the help of standards (they were made only for samples S2 and S3 assuming that the same applies to the rest). Due to the amount of amorphous material present and the low amounts of carbonate produced, an accurate quantitative XRD

analysis was not feasible. For both S2 and S3 three standards were made. Two from the original material with the addition of 5 and 10% pure MgCO_3 and one from the products with 2.5% MgCO_3 .

Figs. 4 and 5 show the XRD pattern of the above samples. The second pattern in each figure is an enlargement of the area inside the red frame. A comparison of the patterns allows one to estimate that the percentage of magnesite formed is around 10 and 5%, respectively. Additionally, from their weights (Table 3), we can observe that sample S2 has gained more weight than S3. This confirms the XRD result of a higher amount of magnesite produced for sample S2. Based on weight gain, samples S4 and S7 had approximately the same fractional carbonation as sample S2.

From the same figures, it can be seen that two kinds of magnesite were detected, magnesite and magnesite ferroan [$(\text{Mg},\text{Fe})\text{CO}_3$]. The formation of the latter can be attributed to incomplete removal of iron during the magnetic separation. Also, since not all of the iron oxide is magnetic and hence some of the iron would have remained. Additionally, iron substitutes for magnesium in the silicates to some extent, which also contributes to the formation of magnesite ferroan.

6. Discussions of previous results

A collaboration involving Los Alamos National Laboratory, Arizona State University, the Albany Research Centre, and the National Energy Technology Laboratory had previously conducted numerous experiments attempting to carbonate ultramafic rock. Most of the work was done on heat pretreated antigorite and lizardite varieties of serpentine. To determine the most suitable conditions for the carbonation reaction

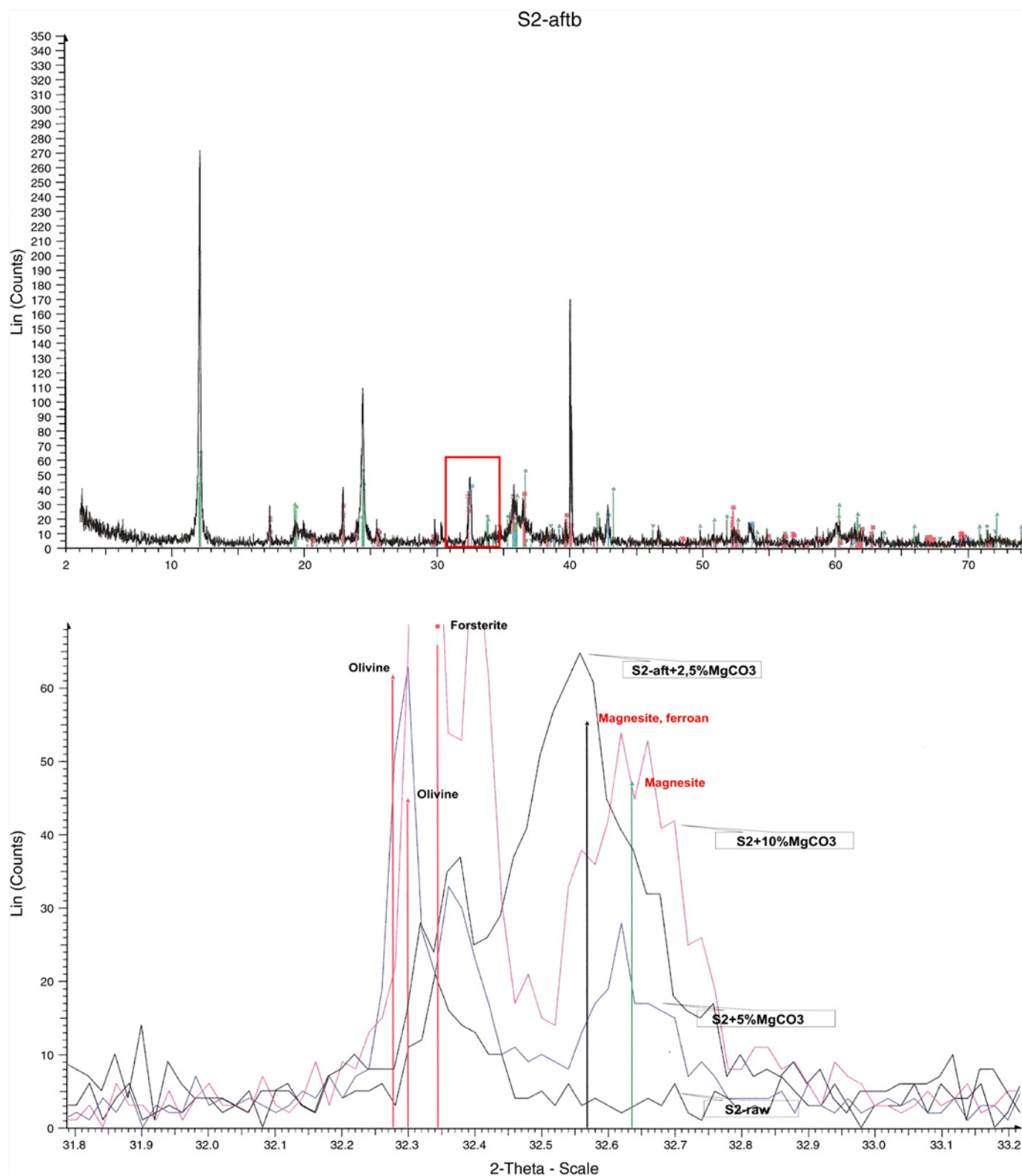


Fig. 4. XRD pattern from sample S2 showing the starting material, that material with both 5 and 10 wt.% MgCO_3 added, and the material following carbonation with 2.5 wt.% MgCO_3 added.

the collaboration members ran experiments at a variety of different pressure and temperature values. Very good results were achieved at the same conditions as the current set of experiments were run, i.e. 158.6 bars, 155 °C, 2 h, etc.

Under these conditions, they found out that the antigorite variety of serpentine carbonated approximately 60% of the stoichiometrically available magnesium in the serpentine sample following heat pre-treatment. The lizardite variety only carbonated 40% under the same

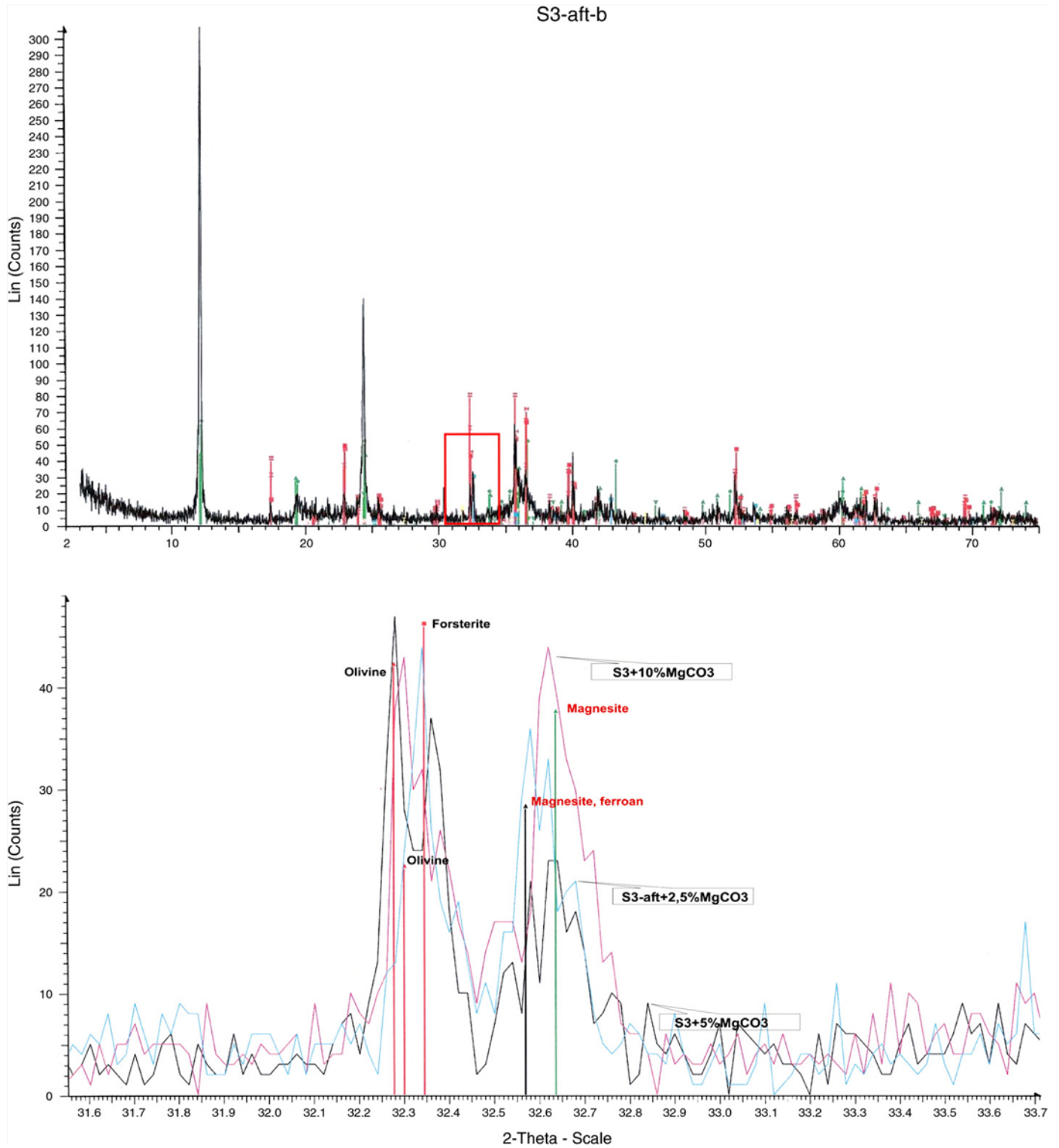


Fig. 5. XRD pattern from sample S3 showing the starting material with both 5 and 10 wt.% MgCO_3 added, and the material following carbonation with 2.5 wt.% MgCO_3 added.

conditions indicating that material variety was of considerable importance in the carbonation reactions. The differences in carbonation extent were repeatable and somewhat surprising as the effects of a particular structural type were assumed to have been destroyed during the heat pre-treatment. However, if not fully destroyed, any residual differences in structure and the free energy associated with it may well explain the differences in carbonation rate/extent (Byler, 2002).

These experiments were also carried out at for similar particles sizes as for the current set of experiments (smaller particle sizes yielded higher reaction rates, but required significant additional grinding energy expenditure).

In contrast to the XRD analysis results of our samples, those of the earlier work showed sharp and substantial magnesite peaks following carbonation that were not present prior to carbonation.

7. Conclusions

The previous research carried out by the collaboration mentioned in the last section showed that heat pre-treatment remains the primary limiting factor in the usability of the process on an industrial scale for the most readily available ultramafic source, serpentine. As the serpentine materials result from an exothermic reaction of hartzburgite, dunite and pyroxenite based material with water, one would expect the serpentinites to be more thermodynamically stable than their source material, and hence a less favorable source material for mineral carbonation. Furthermore, as heat pre-treatment does not impact forsterite, energy intensive heat pre-treatment would not be needed for the forsterite rich rocks available in Greece.

The limited initial carbonation experiments carried out under the current study unfortunately showed relatively low carbonation levels for the hartzburgite and dunite samples studied (the pyroxenite sample did not carbonate at all). This can readily be seen by comparing the XRD patterns, from which it is evident that the composition of the material was not changed significantly. The small weight changes of the samples following the carbonation attempts also confirm the above conclusions. If the material had been successfully carbonated, there should have been a significant increase of its weight.

Longer reaction times could potentially help this situation, as might tuning of the reaction conditions for the particular source material used. Another element that seems to play an important role in the carbonation process is particle size. The smaller the particle size, the higher the percentage of carbonation. Unfortunately, large amounts of grinding energy are required to achieve even smaller particle sizes. There is also the possibility that impurities in our material poisoned the reaction by forming other non-reactive compounds in the solution. Past studies have shown that a solid and largely impermeable shell of magnesium carbonate tends to form on the surface of olivine grains, thereby greatly slowing the speed of the carbonation reaction. Further studies could shed light on these various issues and could also be used to search for catalysts and/or alternative reaction routes to achieve higher conversion levels and reaction rates.

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References

- Byler, D., 2002. CO₂ Sequestration, M.Sc. thesis, New Mexico Institute of Mining and Technology.
- Dabitzias, S., Rassios, A., 2000. Hartzburgites/dunites for high quality olivine products in the Vourinos and Pindos Ophiolite Complexes. 1st Conference of Economic Geology, Mineralogy & Geochemistry, Kozani, 330–340.
- Goff, F., Lackner, K.S., 1998. Carbon dioxide sequestering using ultramafic rocks. *Environ. Geosci.* 5 (3), 89–101.
- Huijgen, W.J.J., Comans, R.N.J., 2003. Carbon dioxide sequestration by mineral carbonation, literature review, Energy research Centre of the Netherlands, ECN-C-03-016, Petten, The Netherlands.
- IPCC—Intergovernmental Panel on Climate Change, 2001. Climate change 2001: the scientific basis. In: Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, M., van der Linden, P.J., Dai, X., Maskell, K., Johnson, C.A. (Eds.), Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK.
- Koukoulas, N., 1998. Distribution of lignite deposits based on the age, quality and their deposits. *Mineral Wealth* 106, 53–68.
- Lackner, K.S., Wendt, C.H., Butt, D.P., Joyce, E.L., Sharp, D.H., 1995. Carbon dioxide disposal in carbonate minerals. *Energy* 20, 1153–1170.
- Lackner, K.S., Butt, D.P., Wendt, C.H., Goff, F., Guthrie, G., 1997. Carbon Dioxide Disposal in Mineral Form: Keeping Coal Competitive. Tech. Report No. LA-UR-97-2094 (Los Alamos National Laboratory).
- Liati, A., Gebauer, D., Fanning, C.M., 2004. The age of ophiolitic rocks of the Hellenides (Vourinos, Pindos, Crete): first U–Pb ion microprobe (SHRIMP) zircon ages. *Chem. Geol.* 207, 171–188.
- O'Connor, W.K., Dahlin, D.C., Nilsen, D.C., Walters, R.P., Turner, P.C., 2000a. Carbon Dioxide Sequestration by Direct Mineral Carbonation with Carbonic Acid. Proceedings of the 25th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, Coal Technology Association, March 6–9.
- O'Connor, W.K., Dahlin, D.C., Nilsen, D.C., Rush, G.E., Walters, R.P., Turner, P.C., 2000b. CO₂ Storage in Solid Form: A Study of Direct Mineral Carbonation. 5th International Conference on Greenhouse Gas Control Technologies, Cairns, Australia, August 13–16.
- Psomas, S., 2006. The end of lignite and the transition towards a new energy period. www.greenpeace.com.
- Ross, J.V., Mercier, J.-C.C., Ave Lallemant, H.G., Carter, N.L., Zimmerman, J., 1980. The Vourinos ophiolite complex, Greece: the tectonite suite. *Tectonophysics* 70, 63–83.
- Teir, S., Kuusik, R., Fogelholm, C.J., Zevenhoven, R., 2007. Production of magnesium carbonates from serpentinite for long-term storage of CO₂. *Int. J. Miner. Process.* 85, 1–15.